CRAY VALLEY
Resins par excellence

APPLICATION BULLETIN

Flexible Foams Based on Poly bd® R45HTLO Resin - Technical Data, Properties and Starting Formulations

Poly bd® resins are liquid, hydroxyl terminated homopolymers of butadiene. The facile reaction of Poly bd® resins with curing agents such as conventional di- and polyisocyanates provides an economical route to the preparation of general purpose elastomers and foams.

The Poly bd® resins are used in castable elastomers, caulks, sealants, membranes, foams, adhesives, coatings, propellant binders, potting and encapsulating compounds, as well as other rubber-fabricated materials.

The unique structure of the Poly bd® resins provides properties which surpass both conventional polyether and polyester urethane systems, as well as conventional, general purpose rubbers. Moreover, the unique compatibility of Poly bd® R45HTLO resin with asphalt allows the formulators to make a unique type of polymer - modified asphalt systems.

Foams based on Poly bd® resins are flexible, with both high hydrophobicity and good resiliency (elastic return). Moreover, due to the polybutadiene backbone, Poly bd® foams exhibit those properties over a wide range of temperatures, especially at low temperatures. This characteristic allows good dynamic behavior over a wide range of temperatures or at high frequencies.

Thus, Poly bd® resins can be used in many different applications, including: gasketing, armrests, damping, carpet backing and asphalt density reduction.

Due to the molecular structure of the Poly bd®, the resulting foamed polyurethane systems exhibit some unique characteristics which are often required by the end users :

Hydrolytic Stability

The hydrophobic backbone of Poly bd® resins imparts excellent hydrolytic stability to the finished product, surpassing that of other types of polyurethane. The polyurethane network of the foam will hence have an outstanding resistance to water. Since water will not wet the Poly bd® based polyurethane, even with a open cells foam, the water will not penetrate easily in the foam. The following table provides data on humid compression set or compression set after humid aging with a basic foam formulation based on Poly bd® resin. Additional data about the MVTR or the low water uptake of Poly bd® resin based formulation in CASE (Coating, Adhesive, Sealant, Elastomer) applications is available upon request.

Chemical Resistance

Polyurethane elastomers based on Poly bd® resins exhibit excellent resistance to aqueous inorganic acids and bases. This characteristic is also attributable to the hydrophobic nature of the polybutadiene backbone. This characteristic is especially beneficial in making armrests (sweat resistance). For gasket applications, Poly bd® could be used in an appliance, where a strong resistance to detergents and other chemicals is often required.

Poly bd® resins are highly hydrophobic, but are compatible with oils and greases.

Oaklands Corporate Center, 468 Thomas Jones Way, Suite 100, Exton, PA 19341
Toll Free 877-871-2729

4922 01/10

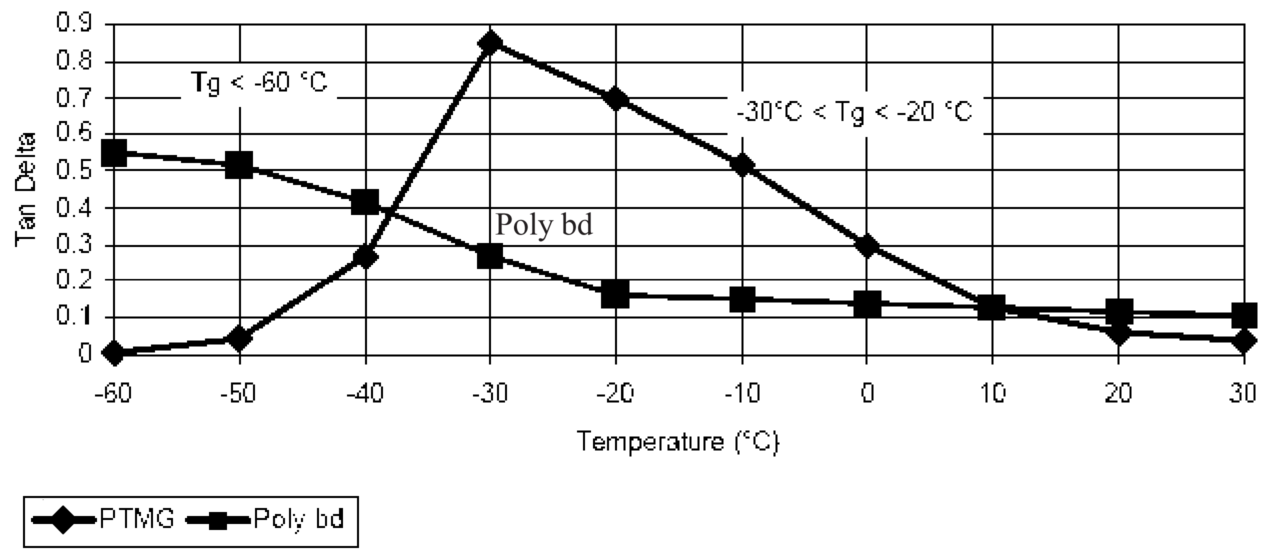
TOTAL

Low Temperature Flexibility : Outside and Dynamic Applications

Polyurethane foams based on Poly bd® resins also exhibit outstanding low temperature properties. This characteristic is attributable to the "rubbery" polybutadiene backbone. Polyurethane formulations derived from Poly bd® resins will have brittle points as low as -70°C (-95°F). In contrast common polyether or polyester polyols have a glass transition temperature around -30°C (-22°F).

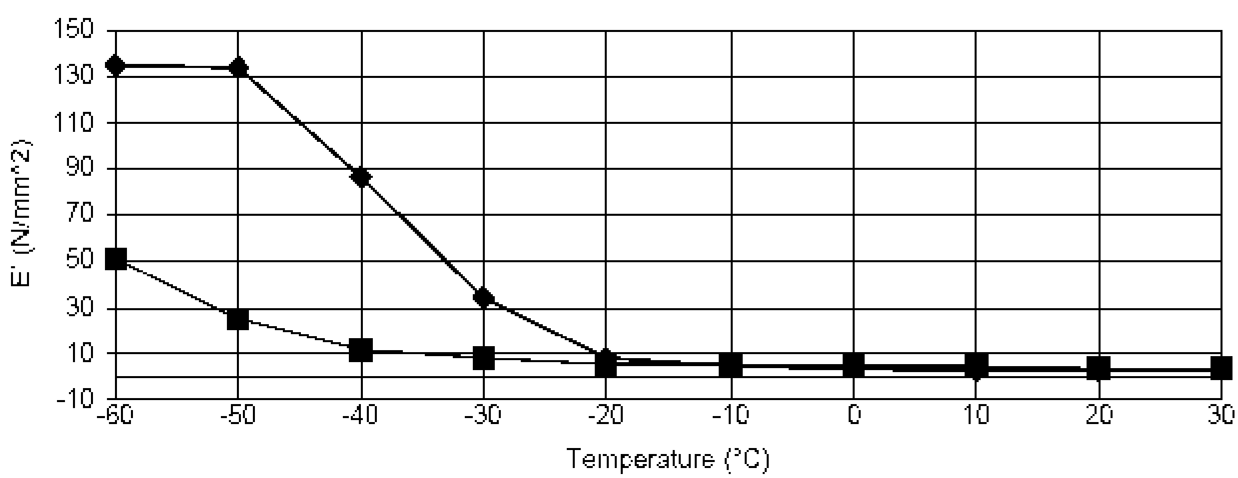
Graph 1 compares the glass transition temperatures of two foams: one based on PTMG, and the other based on Poly bd® resin. This property is very important, especially for the dynamic applications. When the temperature is low, the dynamic properties of regular polyether or polyester based foams are changed because the product becomes rigid. Poly bd® foams will stay flexible and afford good dynamic properties at much lower temperatures (Graph 2). In addition, there is an equivalence between the frequency and the temperature.

Graph 1: Comparison at 100Hz of Glass Transition Temperature



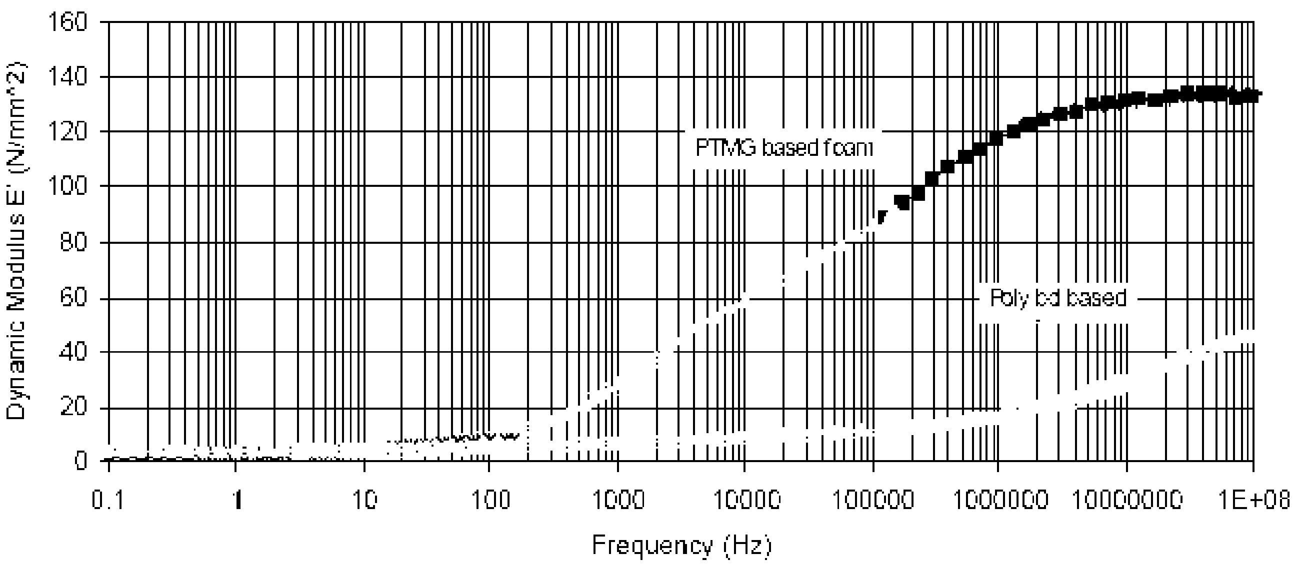
Graph 2: Dynamic Compression Curves

Modulus vs. Temperature (at 100Hz)



For amorphous polymers, a temperature change of 5°C is equivalent to a ten fold change in frequency. Since Poly bd® based PUR foams remain flexible at a lower temperature than conventional PUR, they will maintain good dynamic properties at a much higher frequencies as shown in Graph 3.

Graph 3: Dynamic Comparison: Modulus vs. Frequency (Ref.: -20°C/0.1Hz)



Resilience / Elastic Return
Since the polybutadiene structure is close to rubber, standard foams based on Poly bd® exhibit a very good resilience and a good elastic return similar to rubber. Ball rebound tests done according to ASTM 1564/R gives a resilience of more than 65%. Those foams can hence be considered as high resilience foams.

Adhesion
Once again due to the non polar backbone of the Poly bd® resin, the polyurethane usually exhibits good adhesion to various substrates such as concrete, wood, metallic surfaces and cement.

Poly bd® resin has a low surface tension (36.7 mN/m), and therefore effectively wets many substrates, a condition which is necessary to get a good adhesion. This property is especially interesting for the foamed in place applications, where good adhesion to the substrates is required.

Cellularity
A special feature of Poly bd® based foam is the very tiny cell particle size. These foams are usually open cells, although it is possible to make closed cells using a specific process or when the density of the foam is high.

Low Exotherm
Poly bd® resins when cured with MDI usually exhibit very low exotherms compared to other systems. Temperature measurements were done during and after the cure of foams formulations with more than 2 parts of water. The temperature increase measured during the cure was always below 90°C (laboratory scale sample). This characteristic can help to avoid scorching during cure.

Compatibility With Asphalt and Process Oils
Poly bd® resins, because of their hydrocarbon backbones, are compatible with conventional hydrocarbon oils, chlorinated oils, asphalts and other related low cost materials. Such mixtures can be cured with conventional isocyanates to yield highly extended elastomers or foams.

Starting formulations for asphalt based foams are included in this brochure. Since asphalt has a very low cost, the resulting foam formulations are relatively inexpensive.

Compatibility With Other Polyols

Poly bd® R45HTLO is, in general, compatible to a certain extent with other polyols such as polyether polyols. Depending on the process used (for example a multicomponent machine, or usage of a prepolymer), it is possible to make foams with several different polyols in the formulation.

Formulations

A variety of starting formulations for different potential applications are provided. These formulations are very basic and will need to be modified according to the particular requirements in a given application.

Standard foam formulation: Flexible foam, open cells

Formulation (pbw)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Poly bd® R45HTLO resin	100	100	100	100	100	100	100	100
Niax L1000	2	2	2	2	2	2	2	2
Dabco DC5258	0	0	0.5	0.5	0.5	0.5	0.5	0.5
Toyocat ET	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Toyocat MR	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66
Water	3	3	2	2	2	3	3	3.5
Chain Extender[1]	X	X	EG 3.4	BDO 5	HDO 8	HDO 8	EG/HDO 2/10	EG/HDO 2/16
Polymeric MDI (NCO/OH)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Characteristics	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Density, kg/m^3 (lb/ft^3)	86 5.4	96 6.0	96 6.0	83 5.2	86 5.4	88 5.5	92 5.7	95 5.9
CLD 40%, KPa	15	17	13	10	14	22	29	25
CLD 40% after thermal ageing, KPa	16	20	11	10	15	22	26	27
CLD 40% after humid ageing, KPa	13	16	11	10	14	23	27	23
Compression set, %	6	5	8	9	9	11	13	10
Comp. Set after thermal ageing, %	4	4	8	7	5	7	9	8
Comp. Set after humid ageing, %	4	5	8	7	8	9	10	11
Humid Comp. Set %	6	5	10	8	10	12	18	15
Thermal Conductivity, mW/m.K	40.7	40.7	40	39	39	38	38	33

[1] Chain extender: EG = Ethylene Glycol, BDO = 1,4 Butanediol, HDO = 2-ethyl-1,3 hexanediol
CLD: Compression Load Deflection (according to ISO 3386/1)
Compression set: 22 hours/70°C/50% compression (According to ISO 1856)
Thermal aging=125°C/22 hours, Humid aging=85°C/100% RH/20 hours (ISO 2440)
Humid compression set=50°C/100% RH/22 hours

High density flexible foam using a MDI Prepolymer (for dynamic applications)

Formulation (pbw)	**P1**	**P2**	**P3**	**P4**	**P5**
Poly bd® R45HTLO resin	100	100	100	100	100
1,4 Butanediol		2	4	4	4
Water	0.2	0.2	0.2	0.4	2
Dabco DC1	0.3	0.3	0.3	0.3	0.3
Dabco DC2	0.15	0.15	0.15	0.15	0.15
DBTDL	0.1	0.1	0.1	0.1	0.1
Niax L1000	0.2	0.2	0.2	0.4	1
Lupranat MP102 (NCO/OH=1)	19.4	27.6	35.7	39.5	72.6
Properties					
Density, kg/m^3 (lb/ft^3)	670 (42)	520 (32)	485 (30)	345 (22)	120 (7.5)
Elongation @ break, %	75	88	80	N/A	
Tensile Strength, Mpa (psi)	0.8 (116)	0.9 (130)	1.1 (160)		
% Open Cells	11%	13%	9.5%	81	>90%

Asphalt foams with different densities

Formulation (pbw)	**A1**	**A2**	**A3**	**A4**	**A+**
Poly bd® R45HTLO resin	100	100	100	100	100
Asphalt (grade BP 145, shell)	100	150	150	150	0-200
Water	4	1	0.5	0.75	0-6
Toyacat MR	0.7	0.4	0.4	0.4	0.4-1
Polycat 5	0.1				0.0.2
Niax L1000	1	0.5	0.5	0.5	0-1
Polymeric MDI (NCO/OH=1)	72	26.3	18.7	22.5	
Properties					
Density, kg/m^3 (lb/ft^3) Thermal conductivity (mW/m,K)	110 (6.9) 40	300 (18.7)	550 (34.3)	400 (25.0)	

Surfactant:

Poly bd® resins are very hydrophobic, and are not miscible with water. Hence, when adding water as a blowing agent in a foam formulation, water will not disperse itself in the polyol. It could be possible to find a surfactant that would allow water to be miscible with the Poly bd® resin, but then the cured product will be compatible with water and have a poor water resistance (like a polyether foam). Alternatively, there are some surfactants on the marketplace such as NIAX L1000 (WITCO) or DABCO DC 5258 (Air products) that will allow water to be finely emulsified in the Poly bd® resin. As a result, the water is uniformly dispersed in the Poly bd® resin even though the materials are incompatible.

The following table describes the interfacial tension between Poly bd® R45HT resin and water with or without surfactant :

Surfactant	**None**	**Niax L1000**	**Dabco DC5258**
Interfacial tension (mN/s)	9.6	2.9	0.7

The two surfactants shown can be used in the foam formulations to make a stable inverted emulsion (water in oil, i.e, Poly bd®), and stabilize the cells during foaming. However, the final product is still hydrophobic. Many other surfactant can be used.

Isocyanate:
Although flexible foams may be prepared using TDI, MDI type isocyanates are prefered due to their lower vapor pressure. Only a few trials were done with TDI in our lab.

Polymeric (crude) MDI gives better results than liquid modified MDI. Even better is the use of prepolymers such as LUPRANAT MP102 from BASF, which is a MDI prepolymer with a NCO content by weight of 23%, leading to a foam with a good tear resistance.

The starting formulations demonstrate only foams prepared with regular MDI, and usually with Poly bd® resin as the only polyol. However, it would be possible to modify the formulations with prepolymers or other polyols, for instance halogen containing polyether resins for an improved fire resistance. Some compatibility issues can be solved through the processing, using a multi-component mixing unit.

Chain extender:
Although in CASE applications not all common chain extenders give final products with good properties when used in Poly bd® based formulations, almost all the chain extenders can be used with Poly bd® resin based foam formulations. Ethylene glycol will increase the hardness of the foam, while the use of 1,4 butanediol provides improved softness, and good dynamic properties (low tan Delta)

Catalyst:
In general the same catalysts used in the production of polyether and polyester polyol based flexible foams can be used with Poly bd® resin formulations.

The starting formulations shown on the above table use different catalyst systems, from different suppliers.

Concerning the cream time and the demolding time, some trials where made using a 2 components low pressure mixing machine (SPUHL MD600). The polyol was heated at 50°C. Three different basic formulations where tested :

Poly bd® R45HT resin	100	100	100
Water	2	2	2
Niax L1000	1.5	1.5	1.5
Toyocat MR	0.5	1	1.5

Cured with a polymeric MDI, NCO/OH = 1

Cream Time (sec)	20	12	7
Expansion time (sec)	100	50	35
Demolding time (min)	>10	4	2

Poly bd® / Polyether foams:
A paper titled : New Polyol System Based on Poly bd® Resins for Integral Skin Foams (authors: Flat / Marotel / Nicolescu / Villoutreix was presented during UTECH 94, in Amsterdam.

This paper contains a few starting formulations and properties of flexible foams based on Polyether and Poly bd® polyol mixes, blown with Forane 141b and cured with MDI.